Mechanistic Investigation for the Rechargeable Li-Sulfur Batteries

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Project ID: BAT285

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Overview

Timeline

- Start: 10/01/2018
- Finish: 09/30/2019
- Percentage Complete:50%

Budget

- Funding received in FY18/19: DOE: $300k

Barriers addressed

・Sulfur and Li electrode design to mitigate “shuttle effect”. (A,B,C,D,E)

・Li-S batteries with long calendar and cycle life (C,E)

・Practical high performance sulfur cathode material synthesis (A,C,D,E)

Collaborators

- Johnson Controls Inc.
- University of Washington Seattle.
- Pacific Northwest National Laboratory (PNNL).

- Department of Chemistry, Wuhan University
- Department of Chemistry, Wuhan University of Science and Technology
- Beijing Institute of Technology.
- Institute of Physics, Chinese Academy of Sciences

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Relevance and Project Objectives

- ***Overall Objectives***
  - ✓ ***Mitigation of the "shuttle effect" through understanding the detail mechanism of the sulfur redox reaction.***
  - ✓ ***Exploration of the engineering solutions for the development of long cycle life, high capacity Li-S batteries.***

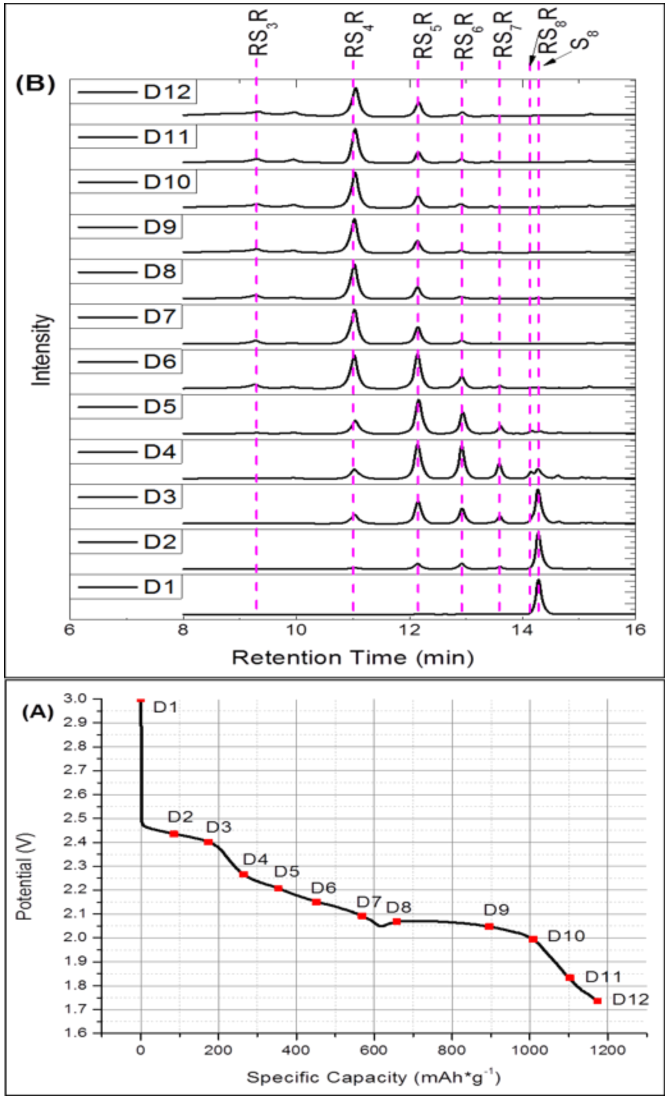
- ***Objectives this period: <u>to enable high energy, high cycle life Li-S batteries through fundamental investigation.</u>***
  - ✓ ***Synthesis of composite sulfur compounds in order to trap dissolved polysulfide ions through strong molecular level interactions.***
  - ✓ ***Exploration of new cathode fabrication method to replace slurry casting.***
  - ✓ ***Taking the advantage of the unique in-situ HPLC-Electrochemical method we developed in the program, to understand the complex mechanism of sulfur interaction in Li-S batteries (to guide the sulfur cathode material, electrolyte synthesis and cell engineering).***
  - ✓ ***Optimization of the in-situ microscopic-electrochemical technique in order to detect dendrite growth during cell operation.***
  - ✓ ***Selection of proper Li containing anode material to mitigate the anode interaction with dissolved polysulfides, thus to limit the "shuttle effect".***

Milestones

Milestone Name/Description	End Date	Status
Complete literature review and preliminary molecular design of polymeric sulfur compounds.	12/31/2018	Completed
Complete screening electrolyte and additives for the Li-S batteries. Start synthesis of polymeric sulfur compounds.	3/31/2019	Completed
Complete preliminary designs of electrode manufacture process and start to explore feasibility for the synthesized polymeric sulfur composite.	6/30/2019	On schedule
Complete the initial design of the electrode manufacture processes and tests of the synthesized polymeric sulfur materials.	9/30/2019	On schedule

Approaches

- *In-situ* High Performance Liquid Chromatography (HPLC)/Mass Spectroscopy(MS)-Electrochemical method. The overall electrochemical and chemical reactions of dissolved polysulfides can be monitored real time.
- *Ex-situ* X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to investigate the surface of sulfur cathode and Li anode to elucidate the surface changes during the Li-S battery operation’
- *In-situ* 3D microscope and electrochemical measurement in a specially designed cell to detect dendrite growth during cell operation.
- Synthesis of polymer sulfur composite material to limit the dissolved polysulfide ion migration.
- Dry method to make high aerial capacity electrodes.
- Extended collaboration with other US and international academic institutions and US industrial partners.



Technical Accomplishments and Progress

- **First quantitative and qualitative determination of dissolved polysulfide ions in Li-S electrolyte.**
- **Comprehensive investigation of Li-S redox reaction mechanism.**
- **Comprehensive investigation of the polysulfide interaction with Li-anode and the inhibitors for the "shuttle effect".**
- **Synthesized polymeric sulfur compound with high rate and good cycle performance.**
- **Developed Li containing anode which does not react with the dissolved polysulfide ions.**
- ***In-situ* electrochemical-laser confocal microscopic cell was made to investigate the surface of Li anode during the cycle of Li-S cell. The Li dendrite growth can be detected real-time during cell operation.**

Strategies to the Mitigation of Negative impacts of Dissolved Polysulfide

- **React with Li anode** — **Low Coulombic Efficiency, Shuttle Effect.**
- **React with Cell Components** — **Capacity Fading, Increase of IR.**
- **React with Electrolyte** — **Electrolyte Decomposition.**

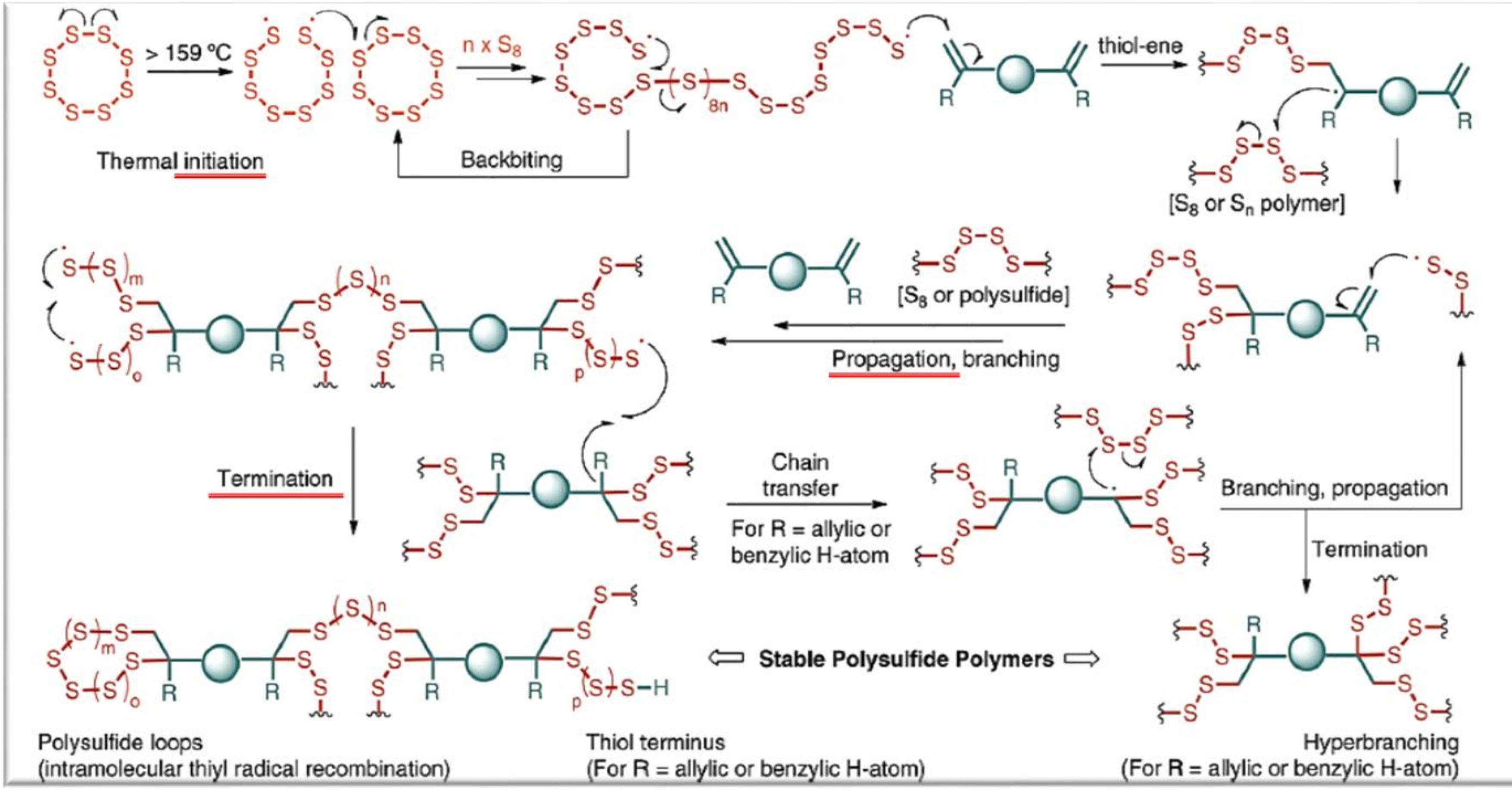
$$S_8 \rightarrow \boxed{S_8^{2-} \rightleftarrows S_7^{2-} \rightleftarrows S_6^{2-} \rightleftarrows S_5^{2-}} \cancel{\xrightarrow{+Li\ metal}} \rightleftharpoons S_4^{2-} + S_3^{2-} + Li_2S_2 \downarrow + Li_2S \downarrow$$

- **Trap soluble polysulfides in porous material.**
- **Selection of solvent – lower solubility.**

Non-reactive anode to polysulfides

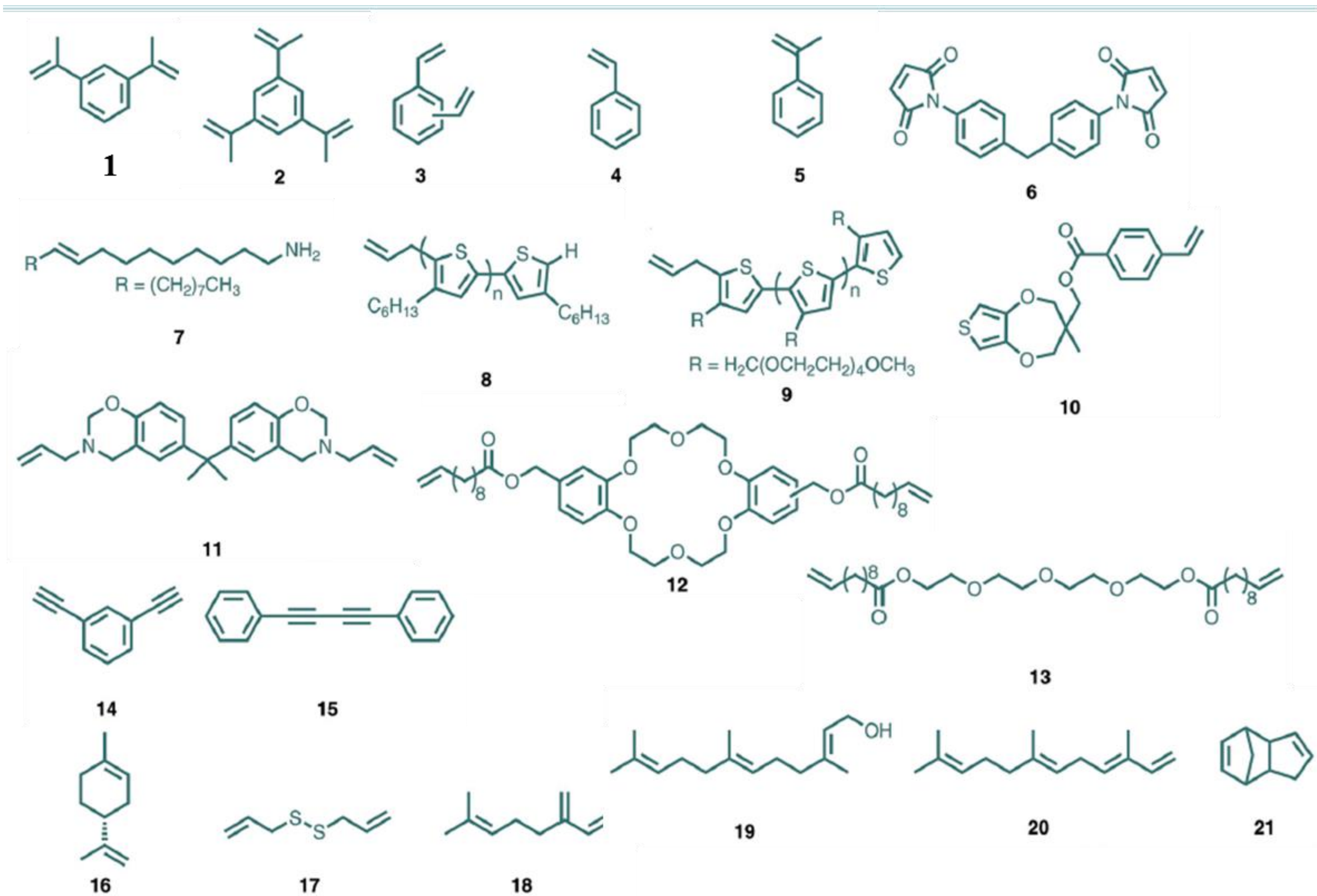
Kinetics vs thermodynamics needs to become a winning game.

Literature Review:
Synthesis Sulfur Containing Polymer- an Example



Chalker et al, ***Green Chem. 2017***,*19,2748*

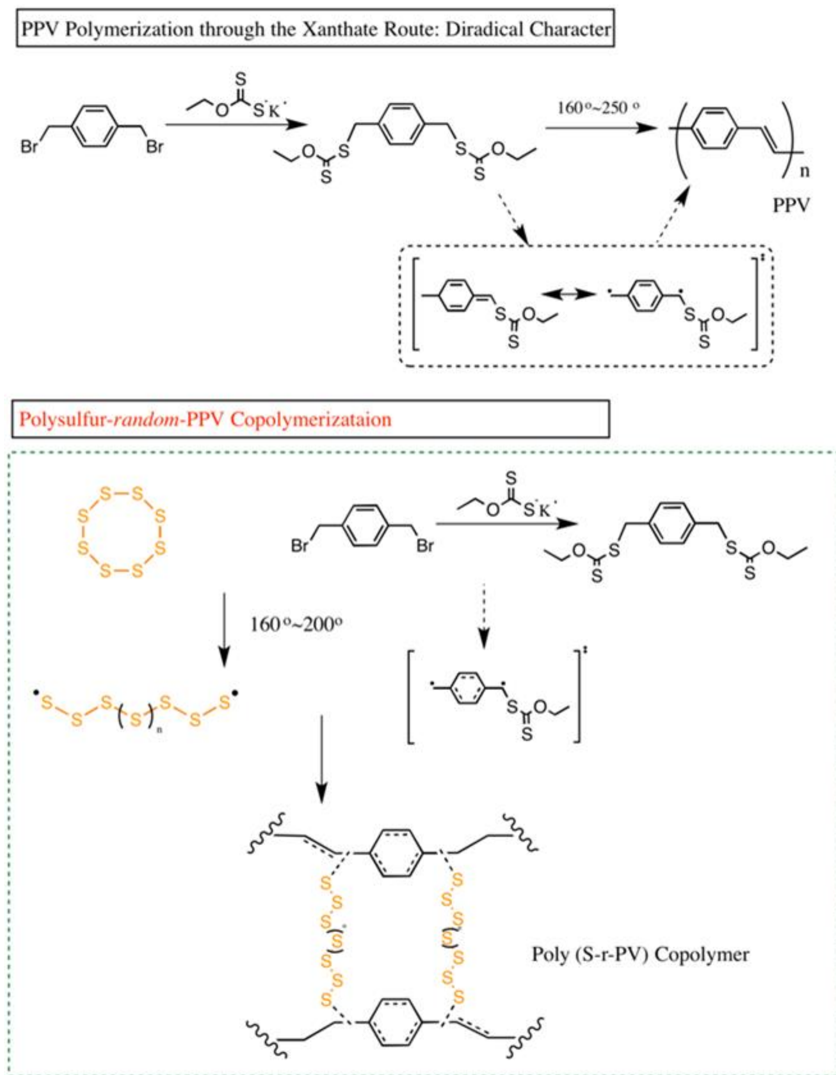
Literature Review:
Examples of unsaturated cross-liners for sulfur-polymer composites



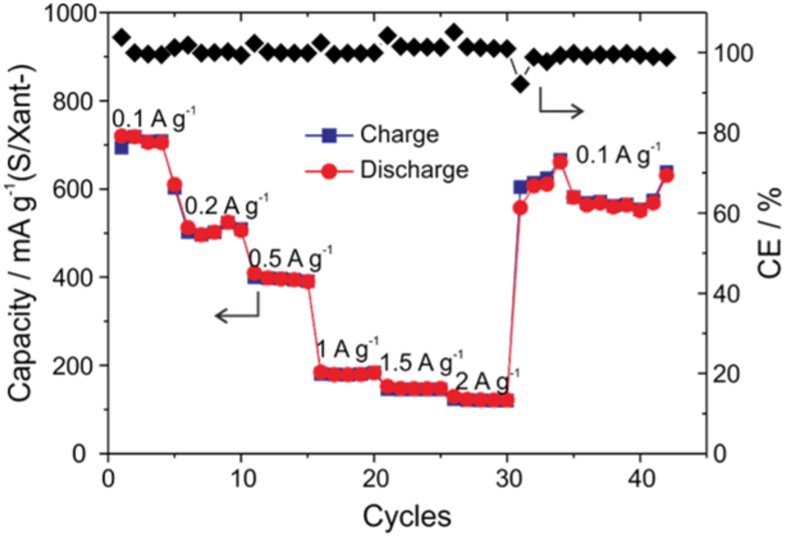
Example of a Sulfur-Polymers (X/Xant) Synthesized

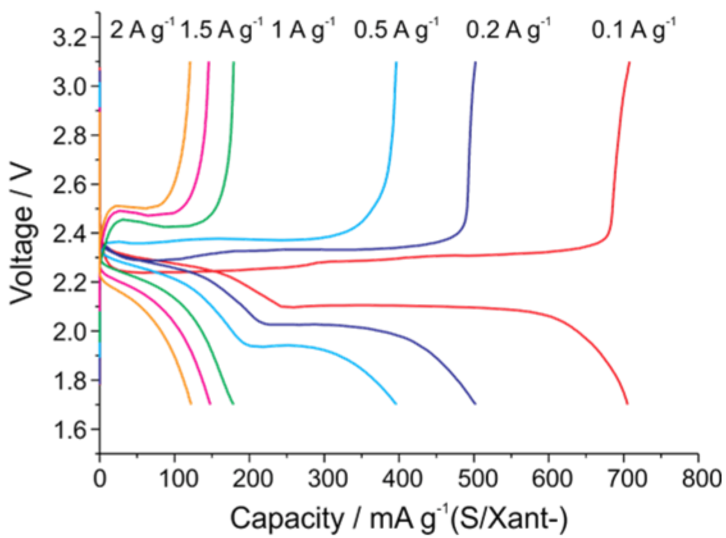
Scheme: Copolymerize sulfur with *p*-Phenylene vinylene to form crosslinked sulfur-rich S/Xant- copolymer.

- ❖ Crosslinked polymer framework
- ❖ Self-protect and confine polysulfide and sulfur dissolution to avoid the detrimental shuttle effects
- ❖ Conjugated conductive PPV help to form fast electron conducting channels and supplement the intrinsic insulating of sulfur



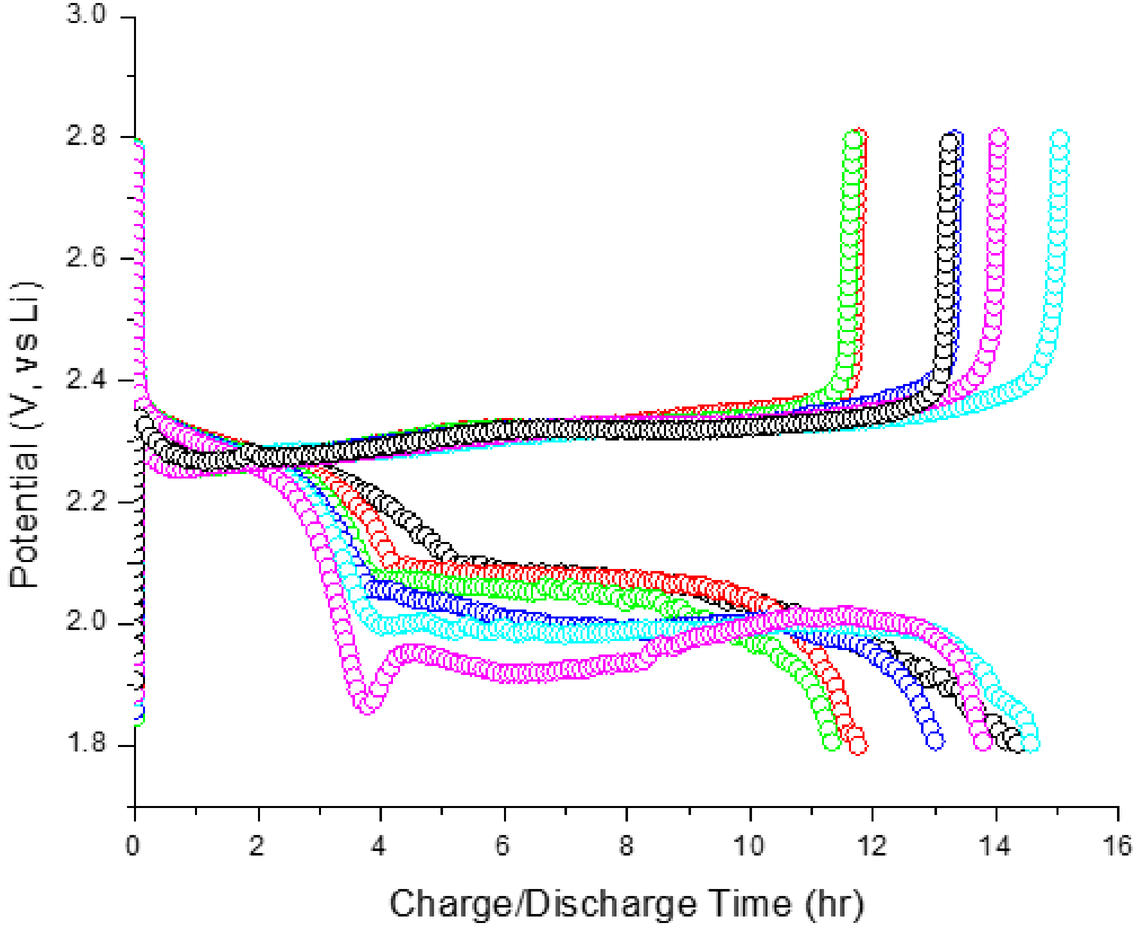
Preliminary Results of the Sulfur-Polymer (X/Xant)





Cycling performances of S/Xant- copolymer (70% sulfur) as cathode.

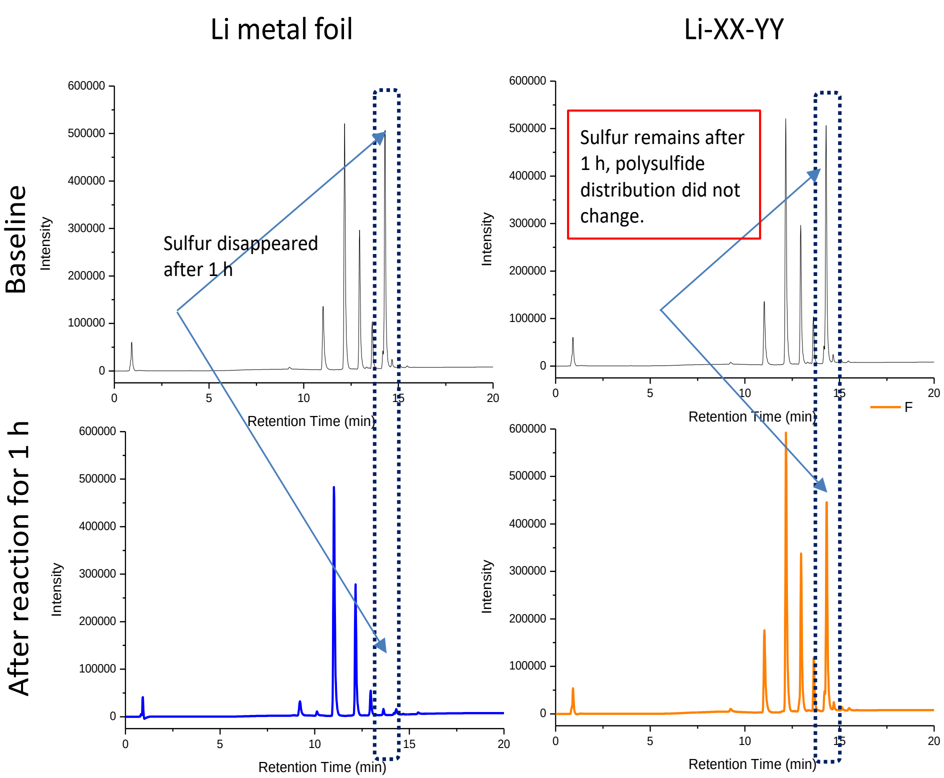
Another Example of Li-S Performance with S-polymer Cathode



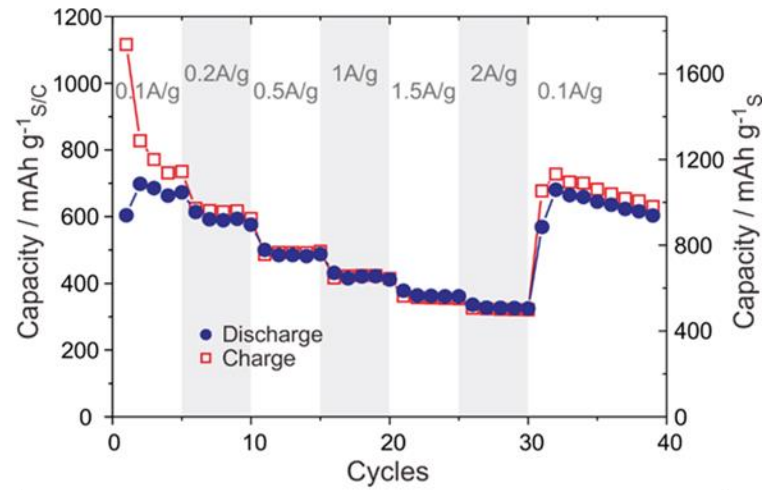
Test results of ten synthesized co-polymer. The control is sulfur cathode with 75% sulfur.

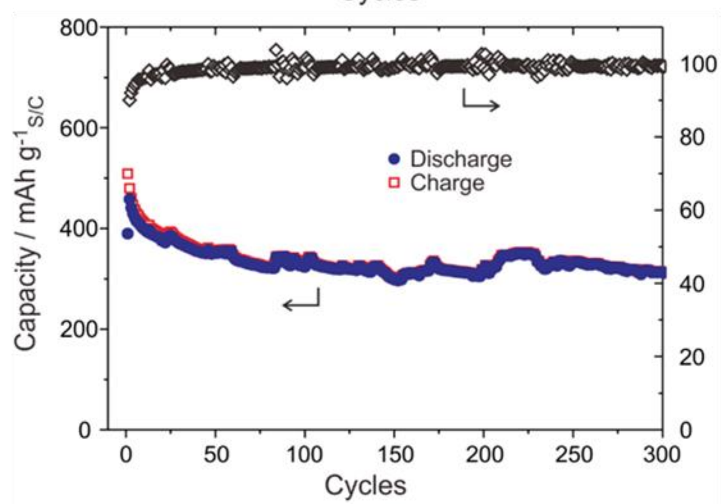
	1st Dischage Capacity (mAh/g)	100th Discharge Capacity (mAh/g)	200th Discharge Capacity (mAh/g)
1	632.9	467.8	340.7
2	671.2	359.3	371.8
3	783.2	374.8	n/a
4	252.3	242.3	201.1
5	1091.8	580.7	n/a
6	210.9	68.5	56.7
7	696.6	323.4	274.8
8	749.9	319.0	178.7
9	227.3	190.3	133.4
10	743.5	374.9	290.2
S8	1364.0	300.9	207.5

Attempts for Alternative Li Containing Anode Material



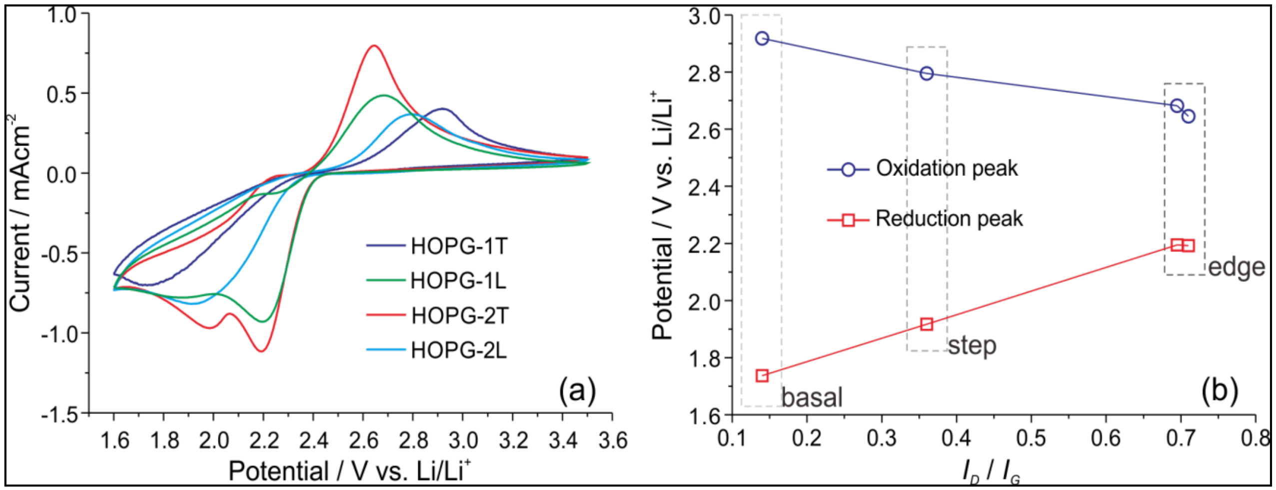
Chemical reaction between Li containing anode materials with dissolved polysulfide ions. The anode materials were put in the electrolyte solution with polysulfide ion. Li-XX-YY was NOT P-Li shown on left.

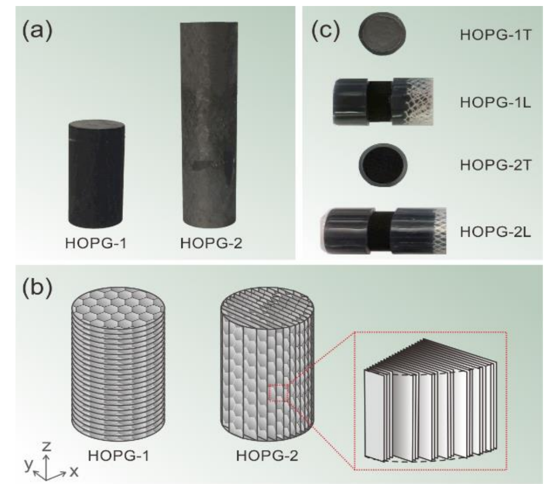




Rate performance of the Sulfur/P-Li coin cell (up); cycling performance of the Sulfur/P-Li at 1 A g^{-1} (low);

The High Aspect Ratio (I_e/I_b) Carbon Should be Used in the Sulfur Cathode, Since Edge Orientation Has high Catalytic Activities

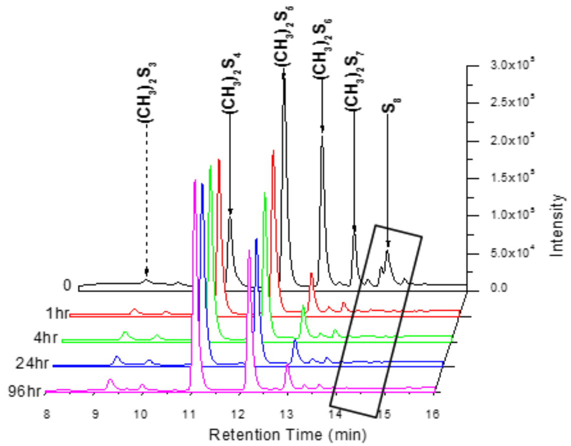




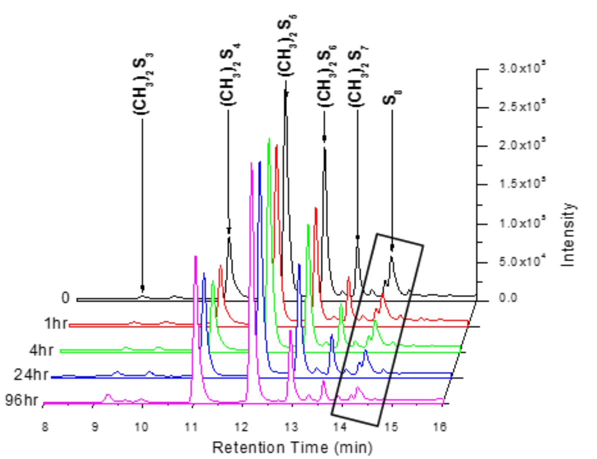
(a) *i*R-free CVs of sulfur electrochemical reduction and oxidation on HOPG-1T (basal plane), HOPG-1L (edge plane), HOPG-2T (edge plane) and HOPG-2L (step plane) at a scan rate of 20 mV/s. (b) The relation between peak potential obtained from (a) and I_D/I_G obtained from Raman analysis.

(a) Photograph of the two HOPG cylinders adopted in this paper. (b) Schematic illustration of the corresponding structures of HOPG-1 and HOPG-2. (c) Photographs of the geometrical configurations of the resulting working electrodes.

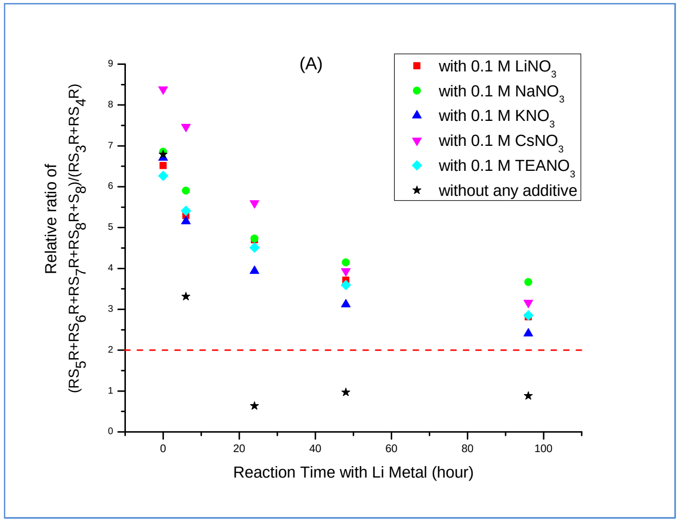
Nitrate additives Can Slow Down the Reaction Between Li and Polysulfides, But Cannot Prevent Such Reaction During Long Term Storage of Li-S Batteries. No Other Additives Are found Better.

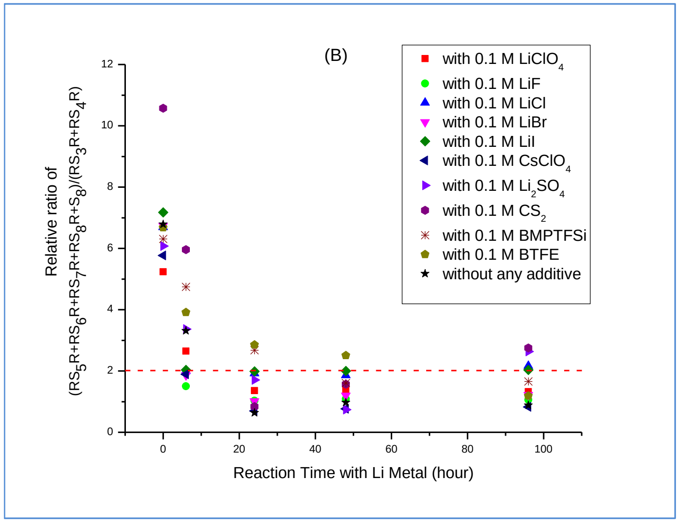


Without addition of $LiNO_3$



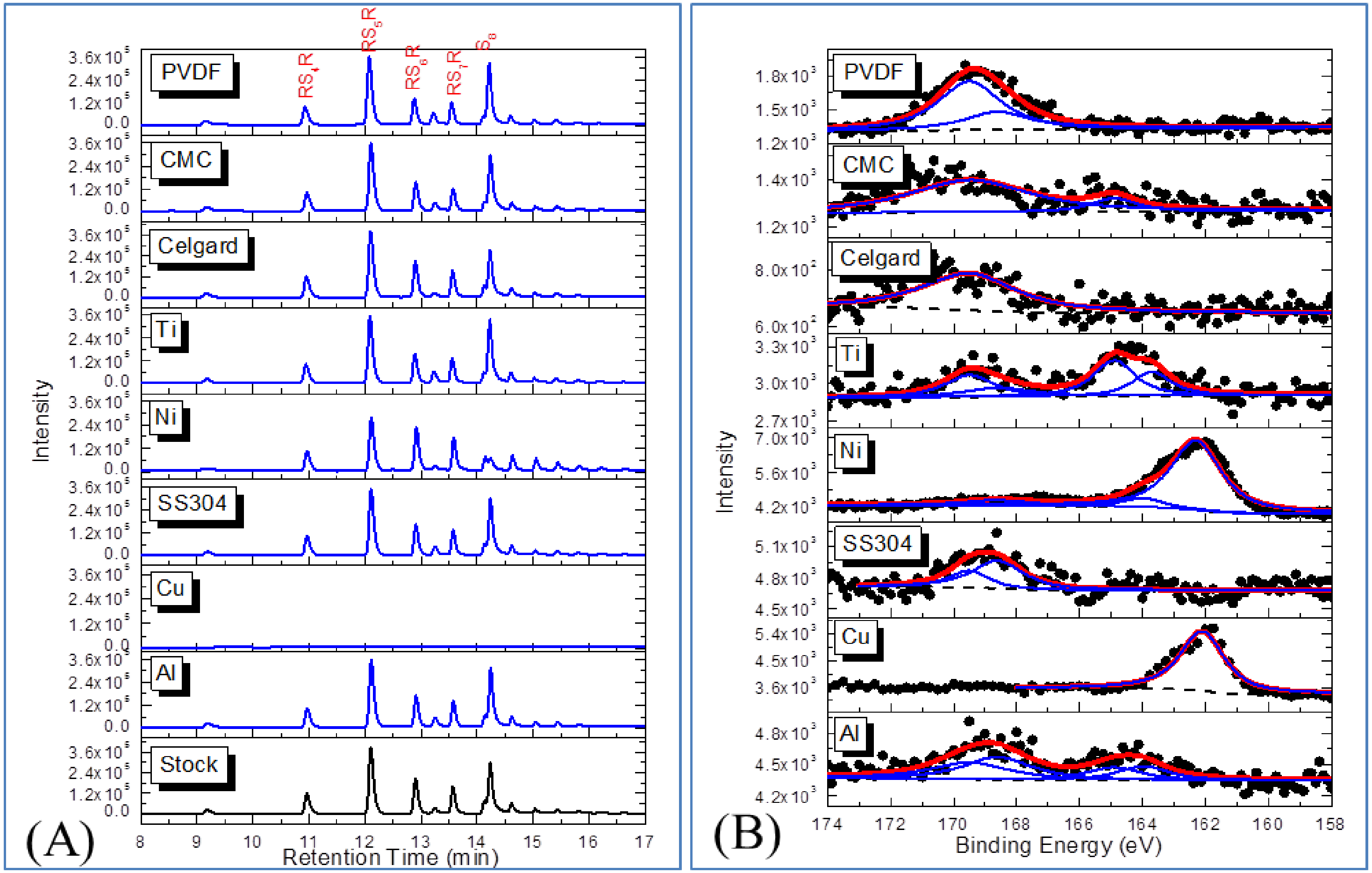
With addition of 0.1 M $LiNO_3$





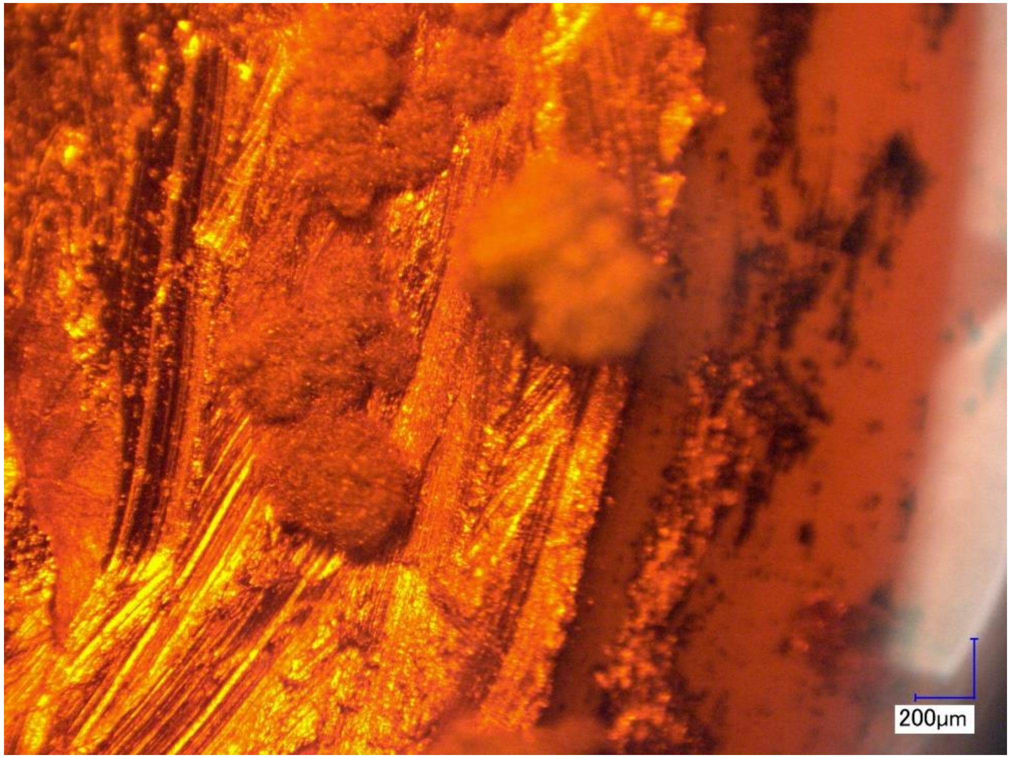
- All Nitrates can slow Li-polysulfide reaction.
- $CsNO_3$ and $NaNO_3$ seem work better than $LiNO_3$
- No other additive was better than nitrate.
- 5-8 sulfur chain length reacted with Li, polysulfide with chain length less than 4 is stable.

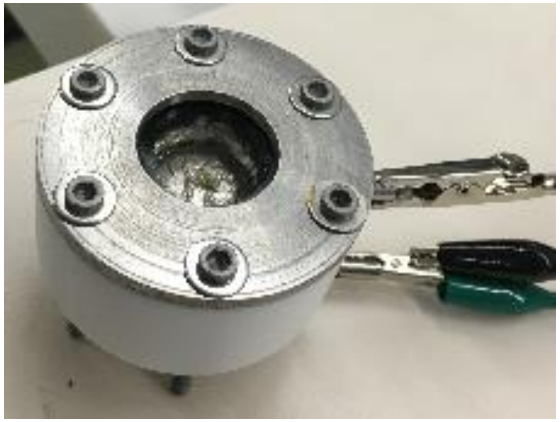
Polysulfide Ions May React with Non-active Cell Components



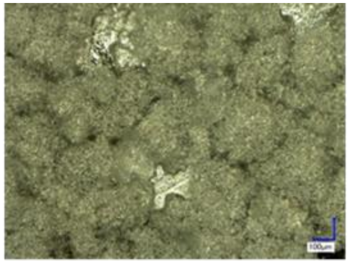
HPLC/UV chromatograms for electrolytes with polysulfides after contacted with different current collectors for 180 days and for stock electrolyte with polysulfides after rest for 180 days at room temperature; (B), XPS measurements of S 2p for five current collectors after contacted with electrolyte (containing 25 mM polysulfides) for 180 days. Black dot: raw data; black dash: baseline; red line: fitted data; blue line: different fitting S 2p species.

Real Time Detection of Dendrite Growth During Li-S Cell Operation

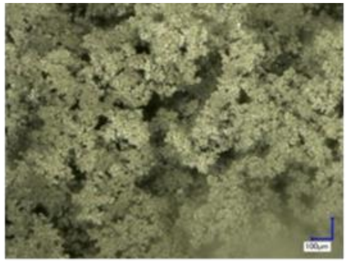




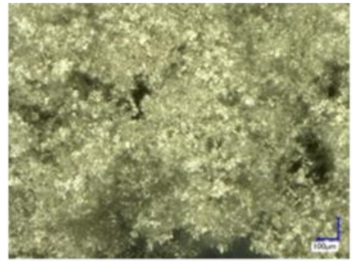
Preliminary Results for the Real Time Dendrite Growth During Li-S Cell Operation



1 M LiBETFSi/DME/DOL, with 0.1 M LiNO3, 2mA/cm2, 1hr

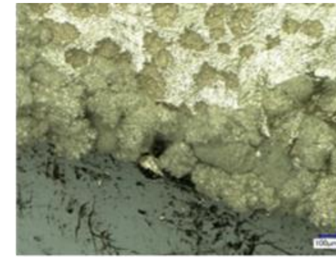


1 M LiClO4/DME/DOL, with 0.1 M LiNO3, 2mA/cm2, 1hr

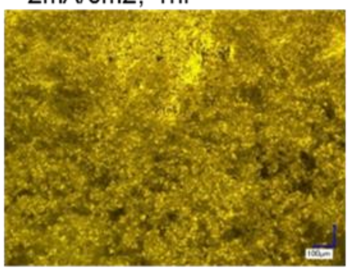


1 M LiDFOB/DME/DOL, with 0.1 M LiNO3, 2mA/cm2, 1hr

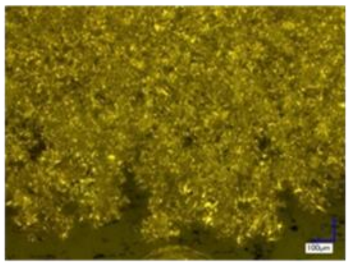
1 M LiTFS/DME/DOL, with 0.1 M LiNO3, 2mA/cm2, 1hr



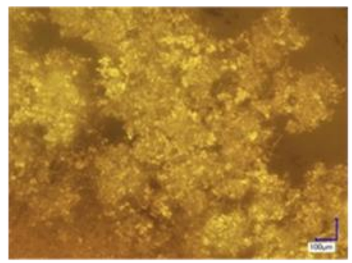
1 M LiTFSi/DME/DOL, with 0.1 M LiNO3, 2mA/cm2, 1hr



1 M LiBETFSi/DME/DOL, with 0.1 M LiNO3 and 0.025M Li2S6, 2mA/cm2, 1hr



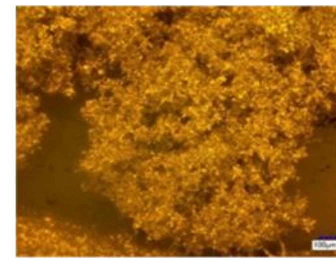
1 M LiClO4/DME/DOL, with 0.1 M LiNO3 and 0.025M Li2S6, 2mA/cm2, 1hr



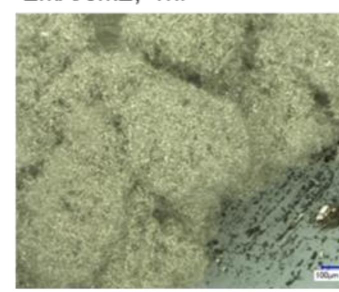
1 M LiDFOB/DME/DOL, with 0.1 M LiNO3 and 0.025M Li2S6, 2mA/cm2, 1hr

1 M LiTFSi/DME/DOL, with 0.05M Cs2CO3, 2mA/cm2, 1hr

1 M LiTFS/DME/DOL, with 0.1 M LiNO3 and 0.025M Li2S6, 2mA/cm2, 1hr



1 M LiTFSi/DME/DOL, with 0.1 M LiNO3 and 0.025M Li2S6, 2mA/cm2, 1hr



1 M LiTFSi/DME/DOL, with 0.05M Cs2CO3, 2mA/cm2, 1hr

Response to last year reviewer's comments

The Project was not reviewed in FY 2018

Collaborations with other institutions and companies

- **Johnson Controls Inc.**
  Optimization of sulfur cathode fabrication.
- **University of Washington Seattle**
  Solid state synthesis of sulfur cathode materials.
- **University of Arkansas**
  Material synthesis and sulfur loading.
- **Pacific Northwest National Laboratory (PNNL)**
  Sulfur loaded carbon cloth electrodes

- **Department of Chemistry, Wuhan University**
  In situ electrochemistry – spectroscopy technique development.
- **Department of Chemistry, Wuhan University of Science and Technology**
  Synthesis of nano particle size sulfur materials
- **Beijing Institute of Technology**
  Sulfur material synthesis
- **Institute of Physics, Chinese Academy of Sciences**
  Electrode structure analysis

Remaining Challenges and Barriers

- It remains a challenge of searching for adequate, effective electrolyte additives or alternative anode materials which can prevent continuous reaction between polysulfide, sulfur and Li anode.
- The lack of adequate additives better than nitrate to prevent the "shuttle effect".
- To limit the diffusivity of dissolved sulfur and polysulfide ions beyond the surface coating and encapsulation, sulfur containing copolymer has been proven effective. Synthesis right structure copolymer which is cost effective and easy for electrode fabrication.
- Sulfur containing electrode with high sulfur loading and decent conductivity.
- Prevent dendrite growth and limit "dead" Li formation.

Any proposed future work is subject to change based on funding levels

Proposed Future Work for *FY 2019* and *FY2020*

▣ FY2019 Q3 Milestone:

Complete preliminary designs of electrode manufacture process and start to explore feasibility for the synthesized polymeric sulfur composite.

▣ FY2019 Q4 Milestone:

Complete the initial design of the electrode manufacture processes and tests of the synthesized polymeric sulfur materials.

FY2020 work:

- ▣ **Continue investigating the mechanism of sulfur redox reaction and searching for adequate additives to mitigate "shuttle effect".**
- ▣ **Complete design and test of the in-situ optical electrochemical method to detect Li dendrite growth during Li-S cell operation real time.**
- ▣ **Continue synthesizing new sulfur containing copolymer materials for performance (cycle life and energy density) improvement.**
- ▣ **Continue exploring alternative S electrode fabrication method to increase the loading of sulfur in engineered carbon structure and explore ways to produce thick sulfur cathode.**
- ▣ **Continuing and enhancing the collaborative research with academic research institutions and industrial partners.**

Any proposed future work is subject to change based on funding levels

Summary

- **Relevance**
  - ✓ *Synthesis and test sulfur containing copolymers to mitigate the migration of dissolved polysulfide ions.*
  - ✓ *Selection of alternative Li containing anode material to reduce the interaction between Li and dissolved polysulfides.*
  - ✓ *Optimization of the in-situ 3D microscopic and electrochemical techniques to detect dendrite growth during cell operation.*
  - ✓ *With the unique in-situ HPLC-Electrochemical method, to further investigate the complex mechanism of sulfur cathode redox reaction in Li-S .*
- **Approaches**
  - ✓ *In-situ electrochemical-HPLC/MS/UV.*
  - ✓ *Ex-situ* X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).
  - ✓ *In-situ electrochemical-3D micro-optical imaging.*
  - ✓ *Exploration of new cathode fabrication method to replace slurry casting.*
- **Technical Accomplishments**
  - ✓ *First quantitative and qualitative determination of dissolved polysulfide ions in Li-S electrolyte.*
  - ✓ *Synthesized polymeric sulfur compound with high rate and good cycle performance.*
  - ✓ *Developed Li containing anode which does not react with the dissolved polysulfide ions.*
  - ✓ *Developed a system to detect Li dendrite growth real-time during cell operation.*
- **Proposed Future work**
  - ✓ *Continue in-situ electrochemistry-HPLC/MS/UV for sulfur redox mechanism study.*
  - ✓ *Optimize real time optical-electrochemical method for Li dendrite growth during Li-S cell operation.*
  - ✓ *Continue developing Li containing copolymer and new electrode fabrication process.*
  - ✓ *Continue searching for new electrolyte including additives to mitigate shuttle effect.*
  - ✓ *Continue developing alternative Li containing Anode to mitigate "shuttle effect" and improve Li-S cycle performance.*

Any proposed future work is subject to change based on funding levels